UPPER AND LOWER BOUNDS FOR RAYLEIGH-SCHRÖDINGER PERTURBATION ENERGIES*

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ABSTRACT

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Variational principles for upper and lower bounds to all even order Rayleigh-Schrödinger perturbation energies are given. The upper bound for the second order energy is just the Hylleraas principle and the upper bounds for energies through 12th order are the same as those used by Knight and Scherr. The general upper bound principle for the (2n)th order energy is equivalent to the variational principle obtained by Sinanoglu for the n-th order wave function, but our principle gives the exact (2n)th order energy when the trial wave function is exact. The lower bounds for the even order energies are generalizations of the lower bound obtained by Prager and Hirschfelder for the second order.

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Introduction

There is increasing interest in the application of perturbation methods to the solution of quantum mechanical problems. In most cases of practical interest, the perturbation equations cannot be solved explicitly so that variational principles are useful for obtaining both the energies and the wave functions in the various orders of perturbation.

In the present paper, variational principles are given for both the upper and lower bounds of the even order energies. For the upper bound principles, our contributions are minor. The principle for the second order energy is well-known[1,2,3], and Knight and Scherr[6] derived similar principles for the even order energies through the twelfth order. Sinanoglu[7] obtained variational principles for the general (2n)th order energies, which are useful for determining the wave functions, but do not reduce to the exact energy when the wave function is exact. The lower bound principle given here is a generalization of the principle for the second order energy given by Prager and Hirschfelder[4]. The application of this principle to problems of practical interest is doubtful due to the difficulty in solving the equation of constraint for any potentials involving the interelectronic distance.

In the work that follows non-degenerate unperturbed states and real wave functions are assumed throughout. Also, the subscripts indicating the state under consideration are omitted to make the notation less cluttered. The zeroth order wave function is normalized to unity, $(\psi^{(0)}, \psi^{(0)}) = 1$. The normalization of each of the other order wave functions, $\psi^{(n)}$, is left arbitrary, except where explicitly discussed in the text.

I. THE UPPER BOUND

The Hylleraas principle is a well known variational principle for the first order Rayleigh-Schrödinger perturbation differential equation, and it provides an upper bound for the second order perturbation energy[2]. In this section the Hylleraas principle is generalized to provide variational principles for all of the higher order perturbation differential equations, both for single and double perturbation problems, and to give upper bounds for all of the even order energies.

A. Single Perturbations

The Rayleigh-Schrödinger perturbation differential equation of order n is[1]

$$(H_0 - \epsilon^{(0)})\psi^{(n)} + (V - \epsilon^{(1)})\psi^{(n-1)} = \sum_{r=2}^{n} \epsilon^{(r)}\psi^{(n-r)} . \quad (1)$$

In the following it will be assumed that the perturbation wave functions of order less than n are known exactly. It will be shown that the perturbation differential equation (Eq. (1)) is the Euler equation corresponding to the variational principle

$$Q^{(n)} = \int \Big[\psi^{(n)} (H_o - \epsilon^{(o)}) \psi^{(n)} + 2\psi^{(n)} (V - \epsilon^{(1)}) \psi^{(n-1)}$$

$$- 2\sum_{r=2}^{n} \epsilon^{(r)} \psi^{(n)} \psi^{(n-r)} + K^{(n)} \Big] d\tau \quad , \tag{2}$$

where $K^{(n)}$ is an arbitrary function which is not subject to the variation as it is independent of $\psi^{(n)}$. Let the unperturbed Hamiltonian, H_o, be of the form

$$H_o = -\tfrac{1}{2}\sum_{i} \nabla_i^2 + U_o \quad , \tag{3}$$

where U_o is a scalar potential and the summation is over the particles in the system. Then Eq. (2) becomes

$$Q^{(n)} = \int \Big[\psi^{(n)} (-\tfrac{1}{2}\sum_{i} \nabla_i^2) \psi^{(n)} + \psi^{(n)} (U_o - \epsilon^{(o)}) \psi^{(n)}$$

$$+ 2\psi^{(n)} (V - \epsilon^{(1)}) \psi^{(n-1)} - 2\sum_{r=2}^{n} \epsilon^{(r)} \psi^{(n)} \psi^{(n-r)} + K^{(n)} \Big] d\tau \,. \tag{4}$$

If it is assumed that $\psi^{(n)}$ vanishes sufficiently rapidly at infinity, Gauss's theorem may be applied to Eq. (4) to give

$$Q^{(n)} = \int \tfrac{1}{2} \sum_{i} \nabla_i \psi^{(n)} \cdot \nabla_i \psi^{(n)} + \psi^{(n)} (U_o - \epsilon^{(o)}) \psi^{(n)}$$

$$+ 2 \psi^{(n)} (V - \epsilon^{(1)}) \psi^{(n-1)} - 2 \sum_{r=2}^{n} \epsilon^{(r)} \psi^{(n)} \psi^{(n-r)} + K^{(n)} \Big] d\tau \quad (5)$$

The Euler equation for this variational principle will be of the form[5]

$$\frac{\partial I}{\partial \psi^{(n)}} - \sum_{i} \left[\frac{\partial}{\partial x_i} \frac{\partial I}{\partial (\psi^{(n)})_{x_i}} + \frac{\partial}{\partial y_i} \frac{\partial I}{\partial (\psi^{(n)})_{y_i}} \right.$$

$$\left. + \frac{\partial}{\partial z_i} \frac{\partial I}{\partial (\psi^{(n)})_{z_i}} \right] = 0 \quad , \qquad (6)$$

where I is the integrand in Eq. (5) and $(\psi^{(n)})_{z_i} = \dfrac{\partial \psi^{(n)}}{\partial z_i}$.

If the explicit form of I as given by Eq. (5) is inserted into Eq. (6) the resulting Euler equation is

$$(-\tfrac{1}{2} \sum_{i} \nabla_i^2 + U_o - \epsilon^{(o)}) \psi^{(n)} + (V - \epsilon^{(1)}) \psi^{(n-1)}$$

$$- \sum_{r=2}^{n} \epsilon^{(r)} \psi^{(n-r)} = 0 \quad , \qquad (7)$$

which is the same as Eq. (1) with H_o given by Eq. (3). The value of $K^{(n)}$ in Eq. (4) is arbitrary. It may be chosen so that when $\psi^{(n)}$ is an exact solution of the differential equation (Eq. (1)) $Q^{(n)}$ will be equal to the (2n)th order perturbation energy, $\epsilon^{(2n)}$. From Eq. (1) for the exact $\psi^{(n)}$

$$(\psi^{(n)}, (H_o - \epsilon^{(o)})\, \psi^{(n)}) = -(\psi^{(n)}, (V - \epsilon^{(1)})\, \psi^{(n-1)}) + \sum_{r=2}^{n} \epsilon^{(r)} (\psi^{(n)}, \psi^{(n-r)}) \quad . \tag{8}$$

When this expression is used in Eq. (2)

$$Q^{(n)} = (\psi^{(n)}, (V - \epsilon^{(1)})\, \psi^{(n-1)}) - \sum_{r=2}^{n} \epsilon^{(r)} (\psi^{(n)}, \psi^{(n-r)}) + \int K^{(n)}\, d\tau \quad . \tag{9}$$

But $\epsilon^{(2n)}$ may be expressed as[1]

$$\epsilon^{(2n)} = (\psi^{(n)}, V\psi^{(n-1)}) - \sum_{i=1}^{n-1} \sum_{j=n-i}^{2n-i} \epsilon^{(j)} (\psi^{(i)}, \psi^{(2n-i-j)}) - \sum_{j=n}^{2n-1} \epsilon^{(j)} (\psi^{(o)}, \psi^{(2n-j)}) \quad . \tag{10}$$

Thus in order to make $Q^{(n)}$ and $\epsilon^{(2n)}$ equal as given by Eqs. (9) and (10)

$$\int K^{(n)} d\tau = -\sum_{i=1}^{n-1} \sum_{j=n-i+1}^{2n-i} \epsilon^{(j)} (\psi^{(i)}, \psi^{(2n-i-j)})$$

$$- \sum_{j=n+1}^{2n-1} \mathcal{E}^{(j)} (\psi^{(o)}, \psi^{(2n-j)}) \quad . \tag{11}$$

The final result is then

$$\tilde{Q}^{(n)} = (\tilde{\psi}^{(n)}, (H_o - \mathcal{E}^{(o)}) \tilde{\psi}^{(n)}) + 2 (\tilde{\psi}^{(n)}, (V - \mathcal{E}^{(1)}) \psi^{(n-1)})$$

$$- 2 \sum_{r=2}^{n} \mathcal{E}^{(r)} (\tilde{\psi}^{(n)}, \psi^{(n-r)}) - \sum_{i=1}^{n-1} \sum_{j=n-i+1}^{2n-i} \mathcal{E}^{(j)} (\psi^{(i)}, \psi^{(2n-i-j)})$$

$$- \sum_{j=n+1}^{2n-1} \mathcal{E}^{(j)} (\psi^{(o)}, \psi^{(2n-j)}) \tag{12}$$

where $\tilde{Q}^{(n)}$ and $\tilde{\psi}^{(n)}$ are approximations to the exact $\mathcal{E}^{(2n)}$ and $\psi^{(n)}$ respectively. When $\tilde{Q}^{(n)}$ is made stationary $\tilde{\psi}^{(n)}$ is the best approximation to $\psi^{(n)}$, and when the state under consideration is the lowest state of a given symmetry $\tilde{Q}^{(n)}$ is an upper bound to the exact $\mathcal{E}^{(2n)}$,

$$\tilde{Q}^{(n)} \geqq \mathcal{E}^{(2n)} \quad . \tag{13}$$

The latter, (Eq. 13) may be shown by writing[1]

$$\tilde{\psi}^{(n)} = \psi^{(n)} + \delta \psi^{(n)} \quad . \tag{14}$$

Then

$$\tilde{Q}^{(n)} = Q^{(n)}_{exact} + (\delta \psi^{(n)}, (H_o - \mathcal{E}^{(o)}) \delta \psi^{(n)})$$

$$+ 2 (\delta \psi^{(n)}, (H_o - \mathcal{E}^{(o)}) \psi^{(n)}) + 2 (\delta \psi^{(n)}, (V - \mathcal{E}^{(1)}) \psi^{(n-1)})$$

$$- 2\sum_{r=2}^{n} \epsilon^{(r)} (\delta\psi^{(n)} , \psi^{(n-r)}) \quad . \tag{15}$$

From the differential equation the last three terms vanish leaving

$$\tilde{Q}^{(n)} - \epsilon^{(2n)} = (\delta\psi^{(n)} , (H_o - \epsilon^{(o)}) \delta\psi^{(n)}) \ . \tag{16}$$

$\delta\psi^{(n)}$ may be expanded in terms of eigenfunctions of H_o which yields

$$\tilde{Q}^{(n)} - \epsilon^{(2n)} = \sum_{k=0}^{\infty} (\delta\psi^{(n)} , \psi_k^{(o)})^2 (\epsilon_k^{(o)} - \epsilon^{(o)}), \tag{17}$$

which is clearly positive when the state considered is the ground state. Whenever the state considered is the lowest of a given symmetry all of the scalar products $(\delta\psi^{(n)} , \psi_k^{(o)})$ with lower states will vanish if it is assumed that $\delta\psi^{(n)}$ has the same symmetry as $\psi^{(o)}$, and the sum in Eq. (17) will still be positive.

The normalization that is used will affect the form of $\tilde{Q}^{(n)}$. If the normalization

$$(\psi^{(o)} , \psi^{(\ell)}) = 0 \qquad (\ell = 1, 2, \ldots n) \tag{18}$$

is used Eq. (12) is simplified somewhat. Under this normalization

$$\tilde{Q}^{(n)} = (\tilde{\psi}^{(n)} , (H_o - \epsilon^{(o)})\tilde{\psi}^{(n)}) + 2(\tilde{\psi}^{(n)} , (V - \epsilon^{(1)}) \psi^{(n-1)})$$

$$- 2\sum_{r=2}^{n-1} \epsilon^{(r)} (\tilde{\psi}^{(n)} , \psi^{(n-r)}) - \sum_{i=1}^{n-1} \sum_{j=n-i+1}^{2n-i-1} \epsilon^{(j)}$$

$$\times (\psi^{(i)} , \psi^{(2n-i-j)}) \quad . \tag{19}$$

The other common normalization,

$$\sum_{k=o}^{\ell} (\psi^{(k)} , \psi^{(\ell - k)}) = 0 \qquad (\ell = 1,2,\ldots n) \quad , \qquad (20)$$

also simplifies the form of $\tilde{Q}^{(n)}$. After some manipulation $\tilde{Q}^{(n)}$ under this normalization becomes

$$\tilde{Q}^{(n)} = (\tilde{\psi}^{(n)}, (H_o - \epsilon^{(o)}) \tilde{\psi}^{(n)}) + 2 (\tilde{\psi}^{(n)} , (V - \epsilon^{(1)})\psi^{(n-1)})$$

$$-2\sum_{r=2}^{n-1} \epsilon^{(r)} (\tilde{\psi}^{(n)} , \psi^{(n-r)}) - \sum_{i=1}^{n-1} \sum_{j=n-i+1}^{n-1} \epsilon^{(j)} (\psi^{(i)}, \psi^{(2n-i-j)}).$$

B. Double Perturbations

Double perturbations may be treated in an entirely analagous manner to that which was used with single perturbations. The Rayleigh-Schrödinger perturbation differential equation of order (r,s) is

$$(H_o - \epsilon^{(o,o)}) \psi^{(r,s)} + (V - \epsilon^{(1,0)}) \psi^{(r-1,s)} + (W - \epsilon^{(0,1)})$$

$$X\psi^{(r,s-1)} = \sum_{j=1}^{n}\sum_{\ell=1}^{s} \epsilon^{(j,\ell)} \psi^{(r-j, s-\ell)} \quad . \qquad (21)$$

In the following it will be assumed that the perturbation wave functions of order less than (r,s) are known exactly. More specifically, wave functions of orders (ℓ,k), (ℓ,s), and (r,k) are known exactly where $\ell < r$ and $k < s$. Then the variational principle for Eq. (21) is

$$\tilde{Q}^{(r,s)} = (\tilde{\psi}^{(r,s)}, (H_o - \epsilon^{(o,o)}) \tilde{\psi}^{(r,s)})$$

$$+2(\tilde{\psi}^{(r,s)}, (V - \epsilon^{(1,0)}) \psi^{(r-1,s)}) + 2(\tilde{\psi}^{(r,s)}, (W - \epsilon^{(0,1)}) \psi^{(r,s-1)})$$

$$- 2\sum_{j=1}^{r}\sum_{\ell=1}^{s} \epsilon^{(j,\ell)} (\tilde{\psi}^{(r,s)}, \psi^{(r-j, s-\ell)}) + \int K^{(r,s)} d\tau . \tag{22}$$

This can be checked by means of the Euler equation as was done for the single perturbations.

The problem remains to make the exact $Q^{(r,s)}$ equal to the exact (2r,2s) order energy, $\epsilon^{(2r,2s)}$, by appropriate choice of $K^{(r,s)}$. If the differential equation for the exact $\psi^{(r,s)}$ is used, the exact $Q^{(r,s)}$ (Eq. (22)) may be modified to give

$$Q^{(r,s)} = (\psi^{(r,s)}, (V - \epsilon^{(1,0)}) \psi^{(r-1,s)})$$

$$+(\psi^{(r,s)}, (W - \epsilon^{(0,1)}) \psi^{(r,s-1)}) - \sum_{j=1}^{r}\sum_{\ell=1}^{s} \epsilon^{(j,\ell)} (\psi^{(r,s)}, \psi^{(r-j,s-\ell)})$$

$$+ \int K^{(r,s)} d\tau . \tag{23}$$

From the general expression for the (2r, 2s) order energy,

$$\epsilon^{(2r,2s)} = (\psi^{(r,s)}, V \psi^{(r-1,s)}) + (\psi^{(r,s)}, W \psi^{(r,s-1)})$$

$$-\sum_{k=0}^{s-1}{}^{*}\sum_{\ell=s-k}^{2s-k}{}^{*}\sum_{i=0}^{r-1}{}^{*}\sum_{j=r-i}^{2r-i}{}^{*} \epsilon^{(j,\ell)} \left(\psi^{(i,k)}, \psi^{(2r-i-j,\ 2s-k-\ell)}\right) \tag{24}$$

(where the asterisk on the sum means the term $i = 0$, $k = 0$, $j = 2r$, $\ell = 2s$ is omitted) it can be seen that to make $Q^{(r,s)}$ and $\epsilon^{(2r,2s)}$ equal as given by Eqs. (23) and (24)

$$\int K^{(r,s)} d\tau = -\sum_{k=0}^{s-1}{}^{*}\sum_{\ell=s-k+1}^{2s-k}{}^{*}\sum_{i=0}^{r-1}{}^{*}\sum_{j=r-i+1}^{2r-i}{}^{*} \epsilon^{(j,\ell)}$$

$$\times \left(\psi^{(i,k)}, \psi^{(2r-i-j,\ 2s-k-\ell)}\right) \quad . \tag{25}$$

Thus the final result is

$$\tilde{Q}^{(r,s)} = \left(\tilde{\psi}^{(r,s)}, (H_o - \epsilon^{(0,0)})\, \tilde{\psi}^{(r,s)}\right)$$

$$+2\left(\tilde{\psi}^{(r,s)}, (V - \epsilon^{(1,0)})\, \psi^{(r-1,s)}\right) + 2\left(\tilde{\psi}^{(r,s)}, (W - \epsilon^{(0,1)})\psi^{(r,s-1)}\right)$$

$$-\ 2\sum_{j=1}^{r}\sum_{k=1}^{s} \epsilon^{(j,k)}\left(\tilde{\psi}^{(r,s)}, \psi^{(r-j,\ s-k)}\right)$$

$$-\sum_{k=0}^{s-1}{}^{*}\sum_{\ell=s-k+1}^{2s-k}{}^{*}\sum_{i=0}^{r-1}{}^{*}\sum_{j=r-i+1}^{2r-i}{}^{*} \epsilon^{(j,\ell)}\left(\psi^{(i,k)}, \psi^{(2r-i-j,\ 2s-k-\ell)}\right), \tag{26}$$

where $\tilde{Q}^{(r,s)}$ and $\tilde{\psi}^{(r,s)}$ are approximations to the exact $\epsilon^{(2r,2s)}$ and $\psi^{(r,s)}$ respectively. When $\tilde{Q}^{(r,s)}$ is made stationary $\tilde{\Psi}^{(r,s)}$ is the best approximation to $\psi^{(r,s)}$, and when the state under consideration is the lowest state of a given symmetry $\tilde{Q}^{(r,s)}$ is an upper bound to $\mathcal{E}^{(2r,2s)}$,

$$\tilde{Q}^{(r,s)} \geqq \mathcal{E}^{(2r,\,2s)} \quad . \tag{27}$$

Various normalization schemes may again be used which will modify the double perturbation equations in much the same way as they modified the single perturbation equations.

II. THE LOWER BOUND

The Thomson principle of electrostatics has been extended[4] to give a lower bound to the second order Rayleigh-Schrödinger perturbation energy. In this section it is extended farther in an analagous manner to give lower bounds for all of the even order energies both for single and for double perturbation problems. In part C of this section the total Schrödinger equation is treated in the same manner and a lower bound is obtained for part of the total energy.

A. Single Perturbations

If $F^{(n)}$ is defined by

$$\psi^{(n)} = F^{(n)}\,\psi^{(0)} \tag{28}$$

the perturbation differential equations take the form[1]

$$\sum_i \nabla_i \cdot (\psi^{(0)^2}\,\nabla_i\,F^{(n)}) = 2\psi^{(0)}(V - \mathcal{E}^{(1)})\,\psi^{(n-1)}$$

$$- 2\psi^{(0)}\sum_{r=2}^{n} \mathcal{E}^{(r)}\,\psi^{(n-r)} \quad . \tag{29}$$

From Eq. (9)

$$\epsilon^{(2n)} = Q^{(n)}_{exact} = (\psi^{(n)} , (V - \epsilon^{(1)})\psi^{(n-1)})$$

$$- \sum_{r=2}^{n} \epsilon^{(r)}(\psi^{(n)} , \psi^{(n-r)}) + \int K^{(n)} d\tau \quad . \tag{30}$$

Therefore, from Eqs. (29) and (30)

$$\sum_i \int F^{(n)} \nabla_i \cdot (\psi^{(0)^2} \nabla_i F^{(n)}) d\tau = 2 \epsilon^{(2n)} - 2\int K^{(n)} d\tau . \tag{31}$$

Using Gauss's theorem and defining $\underset{\sim}{G}_i^{(n)} = -\nabla_i F^{(n)}$,

Eq. (31) becomes

$$\epsilon^{(2n)} - \int K^{(n)} d\tau = - \tfrac{1}{2} \sum_i \int \psi^{(0)^2} \underset{\sim}{G}_i^{(n)} \cdot \underset{\sim}{G}_i^{(n)} d\tau \quad . \tag{32}$$

With the same definition Eq. (29) may be rewritten

$$\sum_i \nabla_i \cdot (\psi^{(0)^2} \underset{\sim}{G}_i^{(n)}) = -2 \psi^{(0)} (V - \epsilon^{(1)}) \psi^{(n-1)}$$

$$+ 2 \psi^{(0)} \sum_{r=2}^{n} \epsilon^{(r)} \psi^{(n-r)} \quad . \tag{33}$$

If $\underset{\sim}{G}_i^{(n)}$ is written as the sum of an approximate field and an error

$$\underset{\sim}{G}_i^{(n)} = \tilde{\underset{\sim}{G}}_i^{(n)} + \delta\, \underset{\sim}{G}_i^{(n)} \tag{34}$$

Eq. (32) becomes

$$\epsilon^{(2n)} - \int K^{(n)}\, d\tau = -\tfrac{1}{2}\sum_i \int \psi^{(0)^2}\, \tilde{\underset{\sim}{G}}_i^{(n)} \cdot \tilde{\underset{\sim}{G}}_i^{(n)}\, d\tau$$

$$- \sum_i \int \psi^{(0)^2}\, \tilde{\underset{\sim}{G}}_i^{(n)} \cdot \delta\, \underset{\sim}{G}_i^{(n)}\, d\tau \quad - \tfrac{1}{2}\sum_i \int \psi^{(o)^2}\, \delta \underset{\sim}{G}_i^{(n)} \cdot \delta \underset{\sim}{G}_i^{(n)}\, d\tau \tag{35}$$

$$= -\tfrac{1}{2}\sum_i \int \psi^{(0)^2}\, \tilde{\underset{\sim}{G}}_i^{(n)} \cdot \tilde{\underset{\sim}{G}}_i^{(n)}\, d\tau \quad - \sum_i \int \psi^{(0)^2}\, \underset{\sim}{G}_i^{(n)} \cdot \delta \underset{\sim}{G}_i^{(n)}\, d\tau$$

$$+ \tfrac{1}{2}\sum_i \int \psi^{(0)^2}\, \delta \underset{\sim}{G}_i^{(n)} \cdot \delta\, \underset{\sim}{G}_i^{(n)}\, d\tau \quad . \tag{36}$$

From the constraint (Eq. (33))

$$\sum_i \nabla_i \cdot (\psi^{(o)^2}\, \delta \underset{\sim}{G}_i^{(n)}) = 0 \quad . \tag{37}$$

Multiplying by $F^{(n)}$ and integrating,

$$\sum_i \int F^{(n)}\, \nabla_i \cdot (\psi^{(o)^2}\, \delta \underset{\sim}{G}_i^{(n)})\, d\tau = 0 \; , \tag{38}$$

and applying Gauss's theorem the following equation is obtained:

$$\sum_i \int \psi^{(0)^2} \; \delta \underline{G}_i^{(n)} \cdot \nabla_i F^{(n)} \; d\tau = 0 \quad . \tag{39}$$

However, $\nabla_i F^{(n)} = -\underline{G}_i^{(n)}$; therefore

$$\sum_i \int \psi^{(0)^2} \underline{G}_i^{(n)} \cdot \delta \underline{G}_i^{(n)} \; d\tau = 0 \quad . \tag{40}$$

Thus upon inserting Eq. (40) into Eq. (36)

$$\epsilon^{(2n)} - \int K^{(n)} d\tau = -\tfrac{1}{2} \sum_i \int \psi^{(0)^2} \underline{\tilde{G}}_i^{(n)} \cdot \underline{\tilde{G}}_i^{(n)} \; d\tau$$

$$+ \tfrac{1}{2} \sum_i \int \psi^{(0)^2} \; \delta \underline{G}_i^{(n)} \cdot \delta \underline{G}_i^{(n)} \; d\tau \quad . \tag{41}$$

Since the second integral on the right is positive it must be true that

$$\epsilon^{(2n)} \geqq -\tfrac{1}{2} \sum_i \int \psi^{(0)^2} \underline{\tilde{G}}_i^{(n)} \cdot \underline{\tilde{G}}_i^{(n)} \; d\tau + \int K^{(n)} d\tau \quad , \tag{42}$$

where $\int K^{(n)} d\tau$ is given by Eq. (11) and $\underline{\tilde{G}}_i^{(n)}$ is subject to the constraint of Eq. (33).

B. Double Perturbations

The treatment of double perturbations is entirely analagous to that of single perturbations. If $F^{(r,s)}$ is defined by

$$\psi^{(r,s)} = F^{(r,s)} \psi^{(0,0)} \tag{43}$$

the perturbation differential equations take the form

$$\sum_i \nabla_i \cdot (\psi^{(0,0)^2} \nabla_i F^{(r,s)}) = 2\psi^{(0,0)} (V - \epsilon^{(1,0)})\psi^{(r-1,s)}$$

$$+ 2\psi^{(0,0)} (W - \epsilon^{(0,1)}) \psi^{(r,s-1)}$$

$$- 2\sum_{j=1}^{r} \sum_{\ell=1}^{s} \psi^{(0,0)} \epsilon^{(j,\ell)} \psi^{(r-j,\, s-\ell)} \quad . \tag{44}$$

From Eq. (23)

$$\epsilon^{(2r,2s)} = Q^{(r,s)}_{exact} = (\psi^{(r,s)}, (V - \epsilon^{(1,0)}) \psi^{(r-1,s)}) +$$

$$(\psi^{(r,s)}, (W - \epsilon^{(0,1)}) \psi^{(r,s-1)}) - \sum_{j=1}^{r} \sum_{\ell=1}^{s} \epsilon^{(j,\ell)}$$

$$\times (\psi^{(r,s)}, \psi^{(r-j,\, s-\ell)}) + \int K^{(r,s)} d\tau \quad . \tag{45}$$

Therefore, from Eqs. (44) and (45)

$$\sum_i \int F^{(r,s)} \nabla_i \cdot (\psi^{(0,0)^2} \nabla_i F^{(r,s)}) \, d\tau =$$

$$2\,\epsilon^{(2r,2s)} - 2\int K^{(r,s)} d\tau \quad . \tag{46}$$

This equation is identical in form to Eq. (31), therefore by the same reasoning as in Sect. IIA it can be deduced that

$$\epsilon^{(2r,2s)} \geq -\tfrac{1}{2}\sum_i \int \psi^{(0,0)^2} \underset{\sim}{G}_i^{(r,s)} \cdot \underset{\sim}{G}_i^{(r,s)} \, d\tau$$

$$+ \int K^{(r,s)} d\tau \quad , \tag{47}$$

where $\int K^{(r,s)} d\tau$ is defined by Eq. (25) and $\tilde{\underline{G}}_i^{(r,s)}$ is an approximation to $-\nabla_i F^{(r,s)}$ subject to the constraint

$$\sum_i \nabla_i \cdot (\psi^{(0,0)^2} \tilde{\underline{G}}_i^{(r,s)}) = -2\, \psi^{(0,0)} (V - \epsilon^{(1,0)})\, \psi^{(r-1,s)}$$

$$-2\, \psi^{(0,0)} (W - \epsilon^{(0,1)})\, \psi^{(r,s-1)} + 2 \sum_{j=1}^{r} \sum_{\ell=1}^{s} \psi^{(0,0)}$$

$$\times\, \epsilon^{(j,\ell)}\, \psi^{(r-j,\, s-\ell)} \quad . \qquad (48)$$

C. The Total Schrödinger Equation

The Schrödinger equation, $(H - E)\Psi = 0$, can be written in the form

$$(\epsilon^{(0)} - H_o)\Psi = (\lambda V + \epsilon^{(0)} - E)\Psi \quad , \qquad (49)$$

where $H_o + \lambda V = H$. If F is defined by the relation

$$\Psi = F\, \psi^{(0)} \quad . \qquad (50)$$

Eq. (49) reduces to

$$\sum_i \nabla_i \cdot (\psi^{(0)^2} \nabla_i F) = 2\, \psi^{(0)} (\epsilon^{(0)} - H_o)\Psi =$$

$$2\, \psi^{(0)} (\lambda V + \epsilon^{(0)} - E)\Psi \qquad (51)$$

which is of the same form as Eqs. (29) and (44). Therefore, this equation may be treated in a similar manner to obtain

$$-\tfrac{1}{2}\sum_i \int \psi^{(0)^2}\, \tilde{\underline{G}}_i \cdot \tilde{\underline{G}}_i \, d\tau \leqq (\Psi, (\epsilon^{(0)} - H_o)\Psi) =$$

$$(\Psi, (\lambda V + \epsilon^{(0)} - E)\Psi) \tag{52}$$

where $\tilde{\underline{G}}_i$ is an approximation to $-\nabla_i F$ subject to the constraint

$$\sum_i \nabla_i \cdot (\psi^{(0)^2} \tilde{\underline{G}}_i) = 2\,\psi^{(0)}\,(\lambda V + \epsilon^{(0)} - E)\Psi \tag{53}$$

This result is of little value as the quantity bounded (Eq. (52)) is only part of the energy, not the total energy, and the constraint involves the exact wave function.

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